Geoderma 300 (2017) 32–43

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Biota and geomorphic processes as key environmental factors controlling soil formation at Elephant Point, Maritime Antarctica

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ARTICLE INFO

Keywords:
Maritime Antarctica
Phosphate minerals
Glacial abrasion
Mineralogy

ABSTRACT

We examined the main soil forming factors affecting the soil composition, soil properties and the associated soil-forming processes at Elephant Point, a small ice-free environment in the South Shetland Islands, Maritime Antarctica. For this purpose, we collected twenty soil samples from each of ten different sites distributed along a linear transect running from the coast to the front of the Rotch Dome glacier. The samples were obtained from surface layers (0–10 cm) and at depth (40–50 cm), although collection was limited in the moraine area by the permafrost table. We determined pH, electrical conductivity, size particle distribution, total organic carbon, total nitrogen and total concentrations of Al, Fe, Ca and P, for physical and chemical characterization of the samples. We also analysed the samples to determine the bioavailability of nutrients and Fe, Al and P partitioning and finally examined them by isotopic ($\delta^{15}N$) and X-ray diffraction (XRD) analysis. The results of the analyses revealed two clear geochemical environments corresponding to the two most extensive geomorphological units in this peninsula: moraine and marine terraces. Soils from the moraine were characterized by alkaline reaction and high quantity of minerals with a low degree of crystallinity, whereas soils from the marine terraces showed acid reaction, high concentration of organometallic complexes and a high diversity of phosphate minerals (taranakite, minyulite, struvite, hydroxylapatite and leucophosphite), which seem to be generated by phosphatization of faecal matter deposited by seabirds and seals. Consequently, biota activity is the most relevant soil differentiating factor in the marine terraces, which add organic matter and activate geochemical cycles. On the other hand, geomorphic processes strongly affected by physical weathering processes such as glacial abrasion (by grinding process), frost shattering, and wind abrasion are the main soil-forming factors in moraine. These forces break up the parent material, transform it and translocate the products formed.

1. Introduction

Knowledge about soil formation and evolution in Antarctica has increased substantially during the last few decades; however, the role of physical and chemical weathering in soil development remains unclear. Some researchers have recently examined the main chemical (Dixon, 2013; Otero et al., 2015a, 2013) and physical (Hall et al., 2002) processes associated with soil formation in cold climates. Among the latter, cryoturbation, wind and stream erosion (Bhatia et al., 2013; Hawkings et al., 2015; Hodson et al., 2004; Wadham et al., 2013), glacial grinding (Cowton et al., 2012; Gengnian et al., 2009; Jari, 1995; Keller and Reesman, 1963a), solifluction (Matsuoka, 2001), sedimentation (Hawkings et al., 2015), salt weathering and freeze-thaw activity (Campbell and Caridge, 1987) are the main processes described, all of which contribute to the heterogeneity of Antarctic soil. Some of the above-mentioned are geomorphic processes which modify the relief and are consequently important soil-forming factors. Moisture conditions are also important in cold regions, and they either limit soil formation (Allen et al., 2001; Thorn et al., 2001) or enhance chemical weathering (Hall, 2004). In areas close to the coast, such as Maritime Antarctica,

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http://dx.doi.org/10.1016/j.geoderma.2017.04.001
Received 28 July 2016; Received in revised form 3 January 2017; Accepted 2 April 2017
Available online 25 April 2017
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chemical weathering may be as important as physical weathering (Anderson et al., 1997; Beyer et al., 2000; Dixon, 2013) and freeze-thaw cycles are more frequent (de Pablo et al., 2014) than in continental Antarctica (Hall, 1997). Chemical weathering is strongly influenced by living organisms, which must adapt to harsh climatic conditions (Otero et al., 2013). Living organisms depend on the existence of ice free areas, which have increased over the last decades as a result of glacial retreat in Livingston Island (Molina et al., 2007), despite recent deceleration of glacier mass loss in the area (Navarro et al., 2013).

Pioneer biota (mainly microorganisms and plants) modifies and adjusts the substrate, thus improving the conditions for new living organisms colonizing these areas. This can create a positive feedback and accelerate soil formation (Moura et al., 2012; Otero et al., 2015a), especially in summer in Maritime Antarctica areas, including the northern tip of Antarctic Peninsula, where the greater availability of water supports chemical weathering processes (Pereira et al., 2013a, 2013b; Simas et al., 2007; Ugolini, 1972). In addition, seabirds and mammals contribute to the establishment and growth of vegetation and enhance mineral weathering due to the high inputs of organic matter, nitrogen and phosphorus via their faecal matter (Pereira et al., 2013b; Schaefer et al., 2008; Simas et al., 2008). The incorporation of organic matter into the mineral soil strongly influences the formation of clay minerals and secondary phosphates, forming the characteristic ornithogenic soils, which are some of the most well developed soils in Maritime Antarctica (Moura et al., 2012).

The original objective of this study was to examine the combined effects of the parent material (Moraines and Marine Terraces) and time (terraces of different ages) on soil formation processes. For this purpose, we established a sampling transect between the coast and the glacier. After observing that soil properties and soil-forming processes were not greatly affected by either parent material or age of the geomorphological units, we decided to refocus the study aims. The final objectives were therefore to identify the main soil forming factors affecting the soil composition, soil properties and the associated soil-forming processes. We analysed several physical and chemical properties of the soil samples taken along the transect, which follows the deglaciation in the environment, including the two most extensive geomorphological units: marine terraces and moraine (Oliva and Ruiz-Fernández, 2017).

2. Material and methods

2.1. Study area

The study was carried out at Elephant Point (62°41′12″ S; 60°51′33″ W), a small peninsula in the westernmost part of Livingston Island (South Shetland Islands, SSI, Antarctica) (Fig. 1). Livingston Island is one of the largest ice free areas in Antarctica (16% of the 818 km^2 is ice free surface), and Elephant Point is included in this ice-free terrain. In this area, the Rotch Dome glacier was significantly more extensive during the Early-Mid Holocene, covering most of the western fringe of Livingston Island until the Late Holocene (Oliva and Ruiz-Fernández, 2017). Consequently, the current ice-free environment at Elephant Point (1.16 km^2) was covered by glacial ice during most of the Holocene. Evidence of this is found in the bedrock plateaus, where some of the blocks are slightly polished and exhibit traces of glacial striae running N–S (Oliva and Ruiz-Fernández, 2015). Subsequently, the glacial retreat that occurred during the Late Holocene, together with the concurrent postglacial isostatic rebound, exposed the low lands of this peninsula, where a sequence of five marine terraces were formed following the glacial retreat (Fretwell et al., 2010; Watcham et al., 2011). The marine terraces thus show a geochronological sequence ranging from 500 years BP (closest to the coast) to 1800 years BP (furthest from the sea) (Table 1). The retreat of the Late Holocene glacier led to formation of a polygenic moraine, with a succession of different ridges due to minor retreats and advances during this time (Oliva and Ruiz-Fernández, 2015). The age of moraine is not as clear as that of marine terraces, although the moraine is known to have been formed later than the terraces, in the last 1.800 years BP.

Field sampling included both of the above-mentioned geomorphological units: marine terraces (MT) and moraine (M). The first five sampling sites correspond to the five marine terraces. The first terrace formed was the farthest from the sea, represented by sample EP5, and the most recent terrace is represented by sample EP1 (closest to the sea) (Table 1 and Fig. 1). The other five sampling sites were further from the sea, in the moraine, and the furthest site (EP10) was very close to Rotch Dome glacier (3 m away). The elevation from the sampling sites ranged from sea level to 55 m·a.s.l. at the internal moraine ridge (Table 1) (Oliva and Ruiz-Fernández, 2017).

2.2. Environmental setting

The climatic conditions at Elephant Point are characteristic of polar oceanic environments. The mean temperature between 2002 and 2010 in the nearby Byers Peninsula was −2.8 °C at 70 m·a.s.l., and the annual precipitation oscillated between 500 and 800 mm, mostly concentrated during the summer season and falling either as rain or snow (Bañón et al., 2013). Freeze-thaw cycles in the ground are also more frequent during this season (de Pablo et al., 2014).

These SSI (South Shetland Islands) are calc-alkaline island arcs (Lee et al., 2004) and are mainly formed by schists, basalts, dacites, conglomerates, rhyolites and andesite (Smellie et al., 1984). The lithology of Elephant Point is mainly formed by weathered basalts, schist, some granodiorites and some shales found in moraine sediments, which are mobilized down-slope by slow mass-wasting processes (Oliva and Ruiz-Fernández, 2017).

Vegetation cover is very sparse and predominantly occurs on the flat marine terraces, where seabirds are present and where they are protected from the wind and from the trapping of penguins (Vera, 2011; Victoria et al., 2013).

The predominant vegetation forms comprise mosses (*Andreaea gainii, Calliergon sarmentosum, Calliergidium austro-stramineum*), lichens (*Usnea antarctica, Usnea aurantiaco-atra, Rhizocarpon geographicum*) and two native vascular plants (*Deschampsia antarctica* and *Colobanthus quitensis*).

2.3. Soil sampling

The initial purpose was to identify any trends in the soil properties relative to the age of the terraces, parent material and the distance from the glacier in the moraine environment. For this purpose, a linear transect was sampled from coast to the glacier in late January 2014 and twenty soil samples were obtained at ten different representative sites at Elephant Point peninsula. Finally, this type of design enabled identification of the main soil-forming factors in the field as well as the associated soil forming processes.

In MT one sampling point was established in each terrace, and in M the same number of sampling points was established at different distances from the glacier. Two samples were taken at each sample point: one from the surface (EP_S: 0–10 cm) and the other at depth (EP_D: 40–50 cm), (Table 1). In accordance with Bockheim et al. (2013), Ramos et al. (2009), Serrano et al. (2008) and Vieira et al. (2010), continuous permafrost was only found in moraine at elevations higher than 30–40 m·a.s.l. However, in MT the compact material was the factor limiting the depth of the sample, which was very homogeneous. The soil samples were stored in PVC boxes until being transported to the laboratory.

2.4. Soil analysis

All samples were sieved through a mesh of 2 mm pore size and analysed in duplicate.

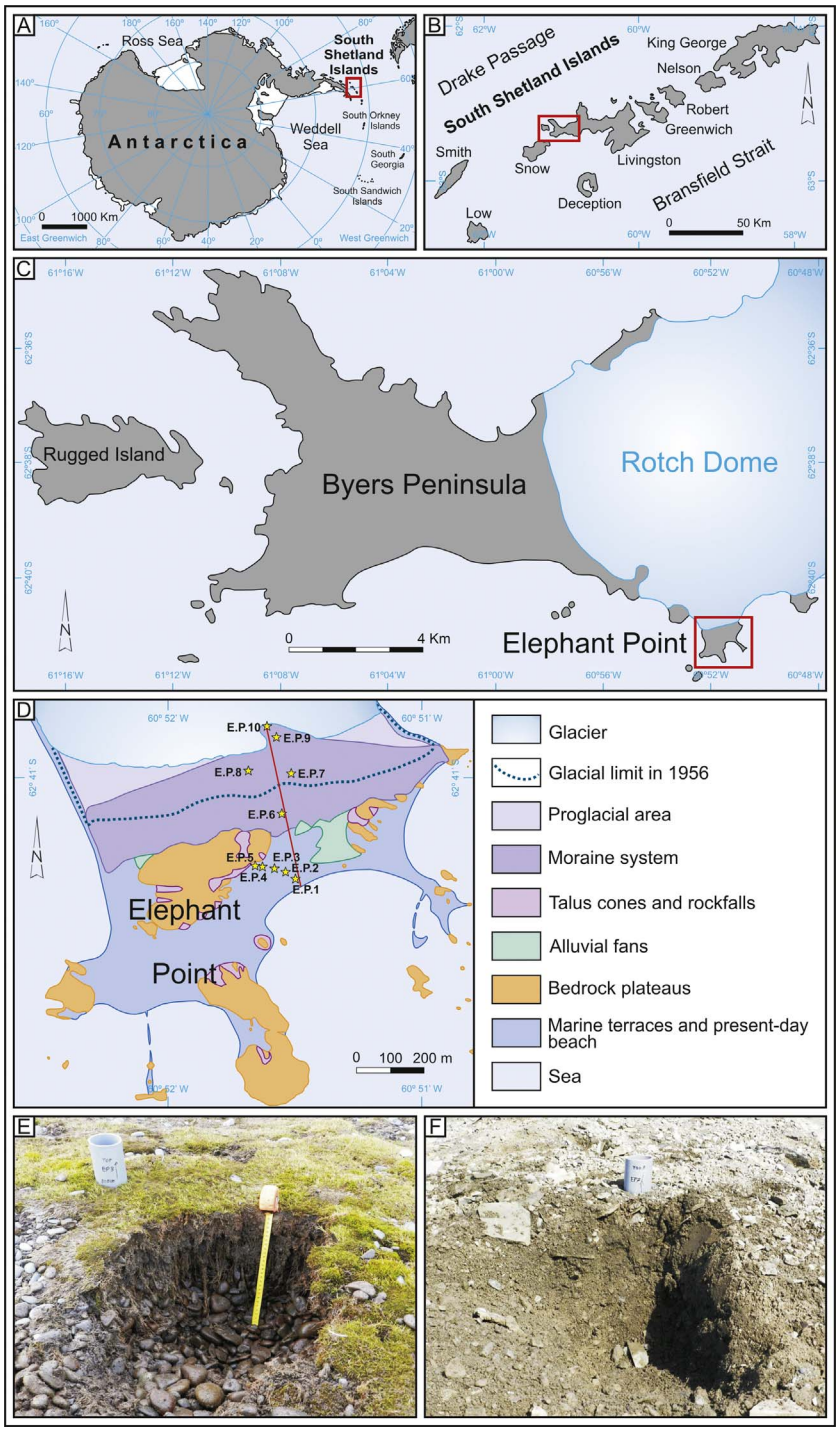

Fig. 1. Location of the study area: (A) location of the South Shetland Islands (SSI) within the Antarctic continent; (B) western fringe of Livingston Island within the SSI; (C) Byers Peninsula and Elephant Point Peninsula within Livingston Island; (D) sampling transect at Elephant Point; (E, F) soil sections EP 3 and EP 8, respectively, showing different type of pebbles on the ground. Rounded pebbles are frequent on the marine terraces, and angular to subangular pebbles are found on the moraine.

2.4.1. Physical and chemical analysis

The pH was determined in water (pH_w) and in 0.1 M KCl (pH_{KCl}), at a ratio of 1:2.5 (Rowell, 1994), and in NaF 1 M (pH_{NaF}), at a ratio of 1:50, for 2 min. Abrasion pH ($pH_{abrasion}$) was determined in the sand fraction. For this purpose, 25 mL of distilled water was added to 10 g of grinded sand (previously washed with Milli-Q water) (Ferrari and Magaldi, 1983). Particle size was determined by the pipette method (Gee and Bauder, 1986). The total organic carbon (TOC), after removal of carbonates with 10% HCl, and total nitrogen (TN) were measured in a LECO CNS-2000 autoanalyzer. The total amounts of Fe (TFe), Al (TAl), P (TP), P sand fraction (TP_{sand}) and Ca (TCa) were extracted in an Ethos Plus microwave lab station by adding 12 mL of a mixture of HNO_3/HCl (3:9, v/v). The efficiency of the extraction process (> 90%) was determined by analysis of certified reference material (Soil SO3).

Three fractions of iron and two of aluminium were extracted: 1) Fe and Al extracted with 0.1 M sodium pyrophosphate (Fe_{pyro} and Al_{pyro}) (Bascomb, 1968); 2) Fe and Al extracted with 0.2 M acid ammonium oxalate at pH 3 (Al_{oxa} and Fe_{oxa}) (Blakemore, 1983); and 3) Fe extracted

Table 1
Geographical description of the sampling sites, together with a general description of the soil sections.

Sample	Depth (cm)	Unit	Elevation (m a.s.l)	Vegetation cover	Geographical Coordinates	Texture, field observations and age of terraces
EP 1S	< 10	MT 5	4	≈ 10%	62°41′12.1″S	Sandy loam. Presence of small lichens and mosses on the surface. Formed over
EP 1D	≈ 40				60°51′33.0″W	500 cal·yr BP
EP 2S	< 10	MT 4	9	≈ 30%	62°41′11.0″S	Loamy sand and sand respectively. Higher organic matter content, mosses and little
EP 2D	≈ 45				60°51′35.0″W	roots. Formed over 1.2 ka cal BP
EP 3S	< 10	MT 3	11	≈ 50%	62°41′10.4″S	Loamy sand. Presence of rounded pebbles. Flat terrain, flooded during some periods.
EP 3D	≈ 45				60°51′36.2″W	Formed over 1.8 ka cal BP
EP 4S	< 10	MT 2	12	≈ 40%	62°41′10.0″S	Sandy. Presence of roots and grey material. Close to semipermanent lagoons. Formed
EP 4D	≈ 40				60°51′37.6″W	over 1.8 ka cal BP
EP 5S	< 10	MT 1	16	≈ 35%	62°41′9.9″S	Sandy. Rounded pebbles in a sandy matrix. Close to an elephant seal colony. Formed
EP 5D	≈ 45				60°51′38.8″W	over 1,8 ka cal BP
EP 6S	< 10	M	18	≈ 5%	62°41′5.9″S	Sandy loam. Presence of angular pebbles next to the moraine slope
EP 6D	≈ 45				60°51′34.3″W	
EP 7S	< 10	M	55	0%	62°41′2.7″S	Sandy loam. No differences between horizons were observed in this homogeneous soil
EP 7D	≈ 55				60°51′34.1″W	section collected from the external moraine ridge.
EP 8S	< 10	M	55	0%	62°41′1.0″S	Sandy loam. These samples were collected from the internal moraine. Evidence of
EP 8D	≈ 45				60°51′38.4″W	glacial abrasion and recent slope activity remobilizing sediments
EP 9S	< 10	M	28	0%	62°40′55.8″S	Sandy loam. High moisture content due to snow melting and thawing of the active
EP 9D	≈ 45				60°51′35.6″W	layer
EP 10S	< 10	M	26	0%	62°40′52.9″S	Sandy loam. Humid environment located only 3 m from the glacier front
EP 10D	≈ 45				60°51′36.8″W	

with sodium dithionite – citrate-bicarbonate (Fe_{dit}) (Mehra and Jackson, 1960). The fractions are considered indicators of different compounds, as follows:

- Fe_{pyro} and Al_{pyro} provide an estimate of the metallo-organic complexes (Bascomb, 1968);
- Fe_{oxa} - Fe_{pyro} provide an estimate of amorphous iron oxides (Fe_{amorp}) (Blakemore, 1983);
- Al_{oxa} - Al_{pyro} provide an estimate of amorphous aluminium oxides (Al_{amorp}) (Blakemore, 1983).
- Fe_{dit} - Fe_{oxa} provides an estimate of crystalline iron oxyhydroxides (Fe_{crys}) (Mehra and Jackson, 1960).

The concentration of C in the pyrophosphate extracts was also determined by a modified version of the method described by Walkley and Black (1934).

Bioavailable macro (P, Ca, Mg, K) and micronutrients (Fe, Co, Cu, Zn and Ni) were extracted with Mehlich 3 extractant (Mehlich, 1984).

Simulation of glacial abrasion by grinding was studied by carrying out a small experiment (Keller and Reesman, 1963a). The sand was separated from eight samples (4 from MT and 4 from M, chosen randomly). The sand was then washed with Milli-Q water and an equal portion of each was ground in a mortar. The ground and unground sand samples were extracted with ammonium oxalate at pH 3 to enable comparison of the concentration of low crystalline phases in each (Blakemore, 1983).

For $\delta^{15}NN$ analysis, 8 samples were chosen randomly (4 from MT and 4 from M). The samples were combusted in an elemental autoanalyzer FlashEA1112 (ThermoFinnigan) and the isotope ratios were determined in a mass spectrophotometer (Deltaplus, ThermoFinnigan).

Partitioning of solid-phase P was determined in fresh samples (2 g) by a sequential extraction method that enable identification of six operationally defined P fractions, which are described as follows (Paludan and Jensen, 1995; Paludan and Morris, 1999):

1. *Adsorbed P:* the most labile and reactive phosphorus (stirring 1 h with Milli-Q water).
2. *P-Fe:* the P associated with reducible Fe and Mn oxyhydroxides (stirring with 0.11 M $NaHCO_3$ and 0.11 M $Na_2S_2O_4$ for 1 h).
3. *P-Al/Clay:* the fraction associated with aluminium and clays (stirring with NaOH 0.1 M for 1 h).
4. *P-HA:* the fraction bound to humic acids (HA) (extracted by precipitation of the HA in the P-Al/Clay supernatant with sulphuric acid, filtration, burning at 520 °C and digestion with HCl 1 M at > 90 °C for at least 10 min).
5. *P-Ca*: the phosphorus associated with calcium (by stirring the residue from P-Al/Clay with HCl 1 M for 1 h).
6. *P-Residual*: the phosphorus bound to recalcitrant compounds as organic matter or which is contained in sand with larger particles (ignition of the residue of P-Ca at 520 °C and subsequent digestion with HCl 1 M at > 90 °C for 10 min).

In all extraction steps, the residue was washed twice with 50 mL of Milli-Q water and centrifuged at 6000 rpm for 15 min (4 °C) to clean any possible residues from the previous extraction.

The contents of Fe, Al, Ca, Mg, K, Co, Cu, and Zn were quantified by atomic absorption spectrometry (PERKIN ELMER 1100B), while P was measured in a spectrophotometer following the procedure described by Murphy and Riley (1962).

2.4.2. Mineralogy

Mineralogical analysis was carried out on clay (< 2 μm), silt (0.05–0.002 mm) and coarse sand fractions (2–1 mm) by X-ray diffraction (XRD). The sand and silt plus clay fractions were then separated by moist sieving and the silt and clay were then separated by decantation (Jackson, 1979). X-ray diffraction (XRD) analysis was carried out on glass slides for oriented aggregates of the clay fraction saturated with Mg^{2+}, and for random powder mounts of unsaturated clays, silt and sand (fine and coarse) fractions. The Mg^{2+} saturated samples were processed as oriented aggregates (Mg) and also solvated in glycerol (Mg-Gli). These sample were also analysed after heating for 3 h at 550 °C and 700 °C (Mg-K550 and Mg-700) (Jackson, 1979).

The XRD patterns were obtained with a Shimadzu XRD 6000 diffractometer (Shimadzu Corporation, Tokyo), using Cu-Kα radiation, with a graphite monochromator and applying 40 kV and a 30 mA current, with a velocity of 1.0°2θ min^{-1} and a step size of 0.02°2θ. The analyses were conducted in the range 2–40°2θ for oriented aggregates and 3–70°2θ for random powder.

2.4.3. Statistical analysis

Owing to the lack of a clear continuous gradient in relation to the age of the terraces and the distance from the glacier, we decided to group the data into four data sets for each main geomorphological unit

Table 2
Mean values and standard deviations obtained from the physical, chemical and isotopic analysis of samples. Values in the same row indicated by the same letter are not significantly different ($p < 5\%$). Underlined variables were analysed by U-Mann-Whitney test, and the other variables by ANOVA followed by a post-hoc Tukey test. * indicates that only samples 2, 4, 7 and 9 were analysed and ** indicates that only samples 4, 5, 7 and 9 were analysed.

Variable	Unit	MT surface		MT depth		M surface		M depth	
		Mean	σ	Mean	σ	Mean	σ	Mean	σ
pH_w		5.3	0.8 a	5.2	0.9 a	8.1	0.4 b	8.2	0.2 b
pH_{KCl}		4.2	0.3 a	4.1	0.4 a	6.7	0.4 b	6.9	0.3 b
pH_{NaF}		8.6	0.3 a	8.8	0.5 ab	9.3	0.2 b	9.3	0.2 b
$pH_{abrasion}$*		8.3	0.1 a	8.3	1.1 a	8.3	0.0 a	8.1	0.1 a
Sand	%	84	8 a	80	18 ab	63	6 b	66	6 b
Silt	%	11	7 a	16	17 ab	27	5 b	26	5 b
Clay	%	5	3 ac	3	1 a	10	3 b	8	1 bc
TOC	%	1.27	0.81 a	0.64	0.27 ab	0.18	0.02 b	0.16	0.01 b
C_{pyro}	%	0.68	0.45 a	0.50	0.40 a	0.16	0.04 a	0.15	0.02 a
TN	%	0.13	0.08 a	0.05	0.03 a	0.01	0.01 b	< L.D	
$\delta^{15}N$**	‰	15.4	3.3	15.3	0.3	4.4	2.0	7.1	1.1
Conductivity	μScm^{-1}	169	138 a	61	45 a	86	52 a	53	19 a
Fe_{pyro}	$mgKg^{-1}$	2754	1072 a	4122	2720 a	147	52 b	319	368 b
Al_{pyro}	$mgKg^{-1}$	989	307 a	1028	775 a	60	70 b	68	11 b
Fe_{amorp}	$mgKg^{-1}$	3957	1004 a	4041	1327 a	4272	465 a	3956	642 a
Al_{amorp}	$mgKg^{-1}$	3132	291 a	3113	1576 a	7479	614 b	6937	1018 b
Fe_{crys}	$mgKg^{-1}$	3922	2662 a	2942	2402 a	2998	340 a	3052	508 a
TFe	$mgKg^{-1}$	49,360	13,439 a	42,960	11,475 a	53,400	3209 a	52,600	1816 a
TAl	$mgKg^{-1}$	29,800	7959 ab	25,680	11,576 a	41,560	4245 b	40,640	2923 b
TCa	$mgKg^{-1}$	33,385	6137 a	29,502	8954 a	48,697	1871 b	48,081	2258 b
P_{Meh}	$mgKg^{-1}$	445	157 a	408	102 a	53	38 b	69	33 b
Co_{Meh}	$mgKg^{-1}$	0.23	0.08 a	0.21	0.13 a	0.45	0.12 b	0.45	0.14 b
Zn_{Meh}	$mgKg^{-1}$	0.46	0.32 a	0.30	0.34 a	1.42	0.77 b	0.80	0.34 b
Cu_{Meh}	$mgKg^{-1}$	2.44	3.46 a	1.74	2.45 a	5.62	1.34 a	4.84	1.42 a
Ni_{Meh}	$mgKg^{-1}$	0.17	0.04 a	0.11	0.08 a	0.29	0.05 a	0.31	0.19 a
Ca_{Meh}	$mgKg^{-1}$	453	399 a	300	415 a	2987	650 b	2948	667 b
Mg_{Meh}	$mgKg^{-1}$	111	87 a	92	127 a	216	35 a	207	43 a
K_{Meh}	$mgKg^{-1}$	228	174 a	133.4	86 a	108	24 a	91	33 a
Fe_{Meh}	$mgKg^{-1}$	37.0	5.5 a	42.8	9.8 a	34.2	2.9 a	31.8	5.2 a
Soluble-P	$mgKg^{-1}$	1.60	2.20 a	0.86	1.20 a	1.60	2.73 a	1.72	3.22 a
P-Fe	$mgKg^{-1}$	319	121 a	398	180 a	29	29 b	34	26 b
P-Al/Clay	$mgKg^{-1}$	1127	665 ab	1605	1051 a	117	56 b	133	36 b
P-HA	$mgKg^{-1}$	104	15 a	113	48 a	18	10 b	22	8 b
P-Ca	$mgKg^{-1}$	421	104 a	434	140 a	535	32 a	553	66 a
$P_{residual}$	$mgKg^{-1}$	165	45 ab	171	68 a	86	13 b	84	15 b
TP_{Sand}	$mgKg^{-1}$	863	123 a	816	407 a	649	79 a	640	98 a
TP	$mgKg^{-1}$	2727	1174 a	2631	1133 a	1207	187 b	1273	132 b

and also considering their depth (MT_s, MT_d, M_s., and M_d) (Table 2). To search for any differences between the two principal geomorphologic areas at Elephant Point and to identify any differences between the samples taken at different depths, we applied ANOVA, the Shapiro-Wilk test and Levene's test (for normally distributed, homoscedastic data) or a non-parametric U-Mann Whitney test (for non normally distributed data). ANOVA was followed by a Tukey test for comparison of all data sets. Differences were considered significant at $p < 0.05$. We also applied Principal Component Analysis (PCA) by implementing a Direct Oblimin test for correlated components. This test enables identification of groups of variables that are correlated with each and with the two main geomorphological units (Fig. 7). The factor scores values (FSV) were calculated for sampling points. We used the 2.0 SPSS statistical software package to carry out all statistical tests, as described by Pallant (2011) and Jolliffe (2002).

3. Results

3.1. General characterization of soils

We did not observe any relationships between soil properties in marine terraces and their ages or between the soil properties in moraine sampling points and the distance from the glacier. The soil composition and properties were very homogeneous in both geomorphological units (marine terraces and moraine). There were no significant differences between either MT_s and MT_d or between M_s and M_d samples. We therefore mainly report and discuss the mean values of the different geomorphological units, taking into account the different depth of samples (Table 2). The description of faecal matter was not taken into account because there was no clear evidence of its presence in MT at the time of the sampling and in M there are no seabird or seal colonies and therefore no faecal matter.

The soils were of coarse texture, varying between sandy and sandy loam. The MT soils were of coarser texture than the M soils (82, 14 and 4% compared with 65, 26 and 9% of sand, silt and clay respectively), and the most notable difference was in the clay fraction (Tables 1 and 2).

Mean pH values (pH_w and pH_{KCl}) differed significantly between the two groups of soils considered (Table 2, Fig. 2A). The MT soil was acidic (MT_S: pH_w 5.3 ± 0.8 and MT_D: pH_w 5.2 ± 0.9), whereas the M soil was slightly alkaline (M_S: pH_w 8.1 ± 0.4 and M_D: pH_w 8.2 ± 0.2). The pH_{NaF} values were higher than 8 and electric conductivity was always very low ($< 150\ \mu S \cdot cm^{-1}$), indicating a low ionic concentration in soil solution (Table 2).

The TOC in the MT soil ranged between 0.22% and 2.53%, and in the M soil between 0.14 and 0.21% (Table 2, and Fig. 2B). The mean concentration of C_{pyro} was also higher in the MT soil (0.08–1.32%) than in the M soil (0.13–0.22%) and also was higher in the surface samples (EP_S) than in the deeper samples (EP_D) (Table 2, Fig. 2B). The TN concentration followed the same pattern as TOC and these variables were strongly positively correlated in each geomorphological unit (MT: $r_s = 0.95$, $p < 0{,}001$; M: $r_s = 0.679$ $p < 0.05$). The TN concentration ranged from 0.01% to 0.25% in MT and from below the limit detection to 0.02% in M. The $\delta^{15}N$ values were very similar in the different

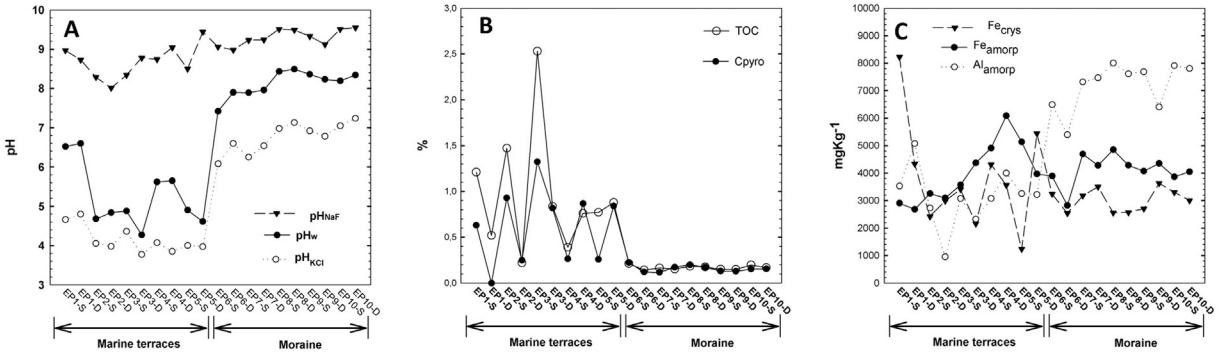

Fig. 2. Spatial variation in the transect of TOC and C_{pyro} (A); pH_w, pH_{KCl}, pH_{NaF} (B); Fe_{amorp}, Al_{amorp} and Fe_{crys} (C).

marine terraces and even at depth, reaching values of 17.7‰, with the lowest being 13‰. The values for M soil were lower, being around 3 times lower than for MT (Table 2).

Spatially, TCa, TAl and TFe showed differences, and the concentrations increased upslope towards the moraine (Table 2). Total Ca differed significantly between the two types of soil, and TAl only differed significantly between MT_D and M. TFe was more homogeneously distributed (Table 2).

The concentrations of metals extracted in sodium pyrophosphate were higher in MT than in M soils. The concentrations of Fe_{pyro} were lower in surface than in deeper samples (2754 and 4122 mg Kg^{-1}, respectively) as in M (147 and 319 mg·Kg^{-1}). Al_{pyro} followed the same pattern as Fe (Table 2). On the other hand, neither Fe_{amorp} or Fe_{crys} were as homogenously distributed across the transect as TFe (Table 2, Fig. 2C). Finally, the concentration of Al_{amorp} was significantly lower in MT (3122 ± 1069 mg·Kg^{-1}) than in M (7806 ± 842 mg·Kg^{-1}) (Table 2, Fig. 2C), but was homogeneously distributed at depth.

The bioavailability of micro and macronutrients was quite high in both units relative to the Mylavarapu categories (Mylavarapu et al., 2014). The concentration of P was high in MT (> 200 mg·kg^{-1}) and intermediate in M (38.1–69.1 mg·kg^{-1}). The concentration of K was intermediate (82.2 mg·kg^{-1}) along the transect, except in MT_S, in which it was high (> 211 mg·kg^{-1}). The concentrations of P and Ca were statistically significantly higher in MT than in M. There were no statistically significant differences in the concentrations of the other micro and macronutrients (Table 2).

Laboratory simulation of glacier abrasion by grinding revealed an increase in Al_{oxa} as well as Fe_{oxa} and Si_{oxa} in the ground samples. There was a mean increase of 44% and 19% for Al_{oxa} in MT and M (respectively) and a 72% and 67% for Si_{oxa} in MT and M (respectively) (Table 2, Fig. 2). There were no statistically significant differences in the concentrations of Al, Fe or Si between the units.

3.2. Total phosphorus and partitioning in soil

Total P (TP) was approximately two times higher in the MT unit (from 1348 to 4799 mg·kg^{-1}) than in the M unit (from 1006 to 1480 mg·kg^{-1}), and the concentration of TP was significantly higher in MT than in M (Table 2). On the other hand, TP_{sand} showed a basal level along the transect without significant differences neither between geomorphological units nor in depth (Table 2).

Phosphorus partitioning showed two main fractions linked to the geomorphologic units. The dominant fraction in MT was P-Al/Clay (from 34% to 66%; Fig. 2), whereas P—Ca was the dominant fraction in M (57%–75%). The concentrations of adsorbed P were very low in both cases, representing < 0.2% of the total P. The concentration of P associated with Fe and HA was higher in MT (from 10.1% to 18.6% and from 3.1% to 6.7%, respectively) than in M (from 1.3% to 8% and from 1.2% to 3.4%, respectively). Finally, although the recalcitrant P fraction represents 7.4% in MT and 10.6% in M, the amount of residual P was higher in MT (Table 2, Fig. 4). The P partitioning of phosphorus can be summarized as follow:

- MT unit: P-Al/Clay ⋙ P-Ca > P-Fe > P-residual > P-HA ≫ Adsorbed-P
- M unit: P-Ca ⋙ P-Al/Clay > P-residual > P-Fe ~ P-HA - ≫ Adsorbed P

3.3. Mineralogy

The clay mineralogy composition was clearly different in the two units considered (Fig. 5). MT soils contained a higher proportion of phosphate minerals such as struvite (0.590 nm, 0.560 nm and 0.269 nm), leucophosphite (0.670 nm, 0.550 nm, 0.470 nm), minyulite (0.690 nm) taranakite (1.54 nm, 0.760 nm) and hydroxylapatite (0.281 nm, 0.277 nm, 0.271 nm). On the other hand, the M soils contained a higher abundance of secondary minerals such as vermiculite, chlorite (1.42 nm), kaolinite (0.71 nm) and talc (0.94 nm), as well as interstratified minerals such as chlorite/vermiculite (2.91 nm) (see Fig. 6 for more detail). However, there were no phosphate minerals in the clay fraction of the M soil (Fig.5).

Sand and silt fractions were dominated by primary minerals in both units (Fig. 5), with plagioclase (0.688 nm, 0.644 nm, 0.403–0.405 nm, 0.374 nm, 0.388 nm, 0,366 nm, 0.334 nm, 0.327 nm and 0.319–0.320 nm) and quartz (0.427–0.425 nm) being particularly important.

The silt fraction contained a combination of minerals found in MT and M clays. Some phosphate minerals and secondary minerals were observed such as those found in M clays (Fig. 5). Iron oxides were also identified in silt fraction of the two units. Magnetite (0.252 nm) and maghemite (0.252) were identified in MT, and goethite was detected in Mt. (0.417 nm).

Finally, XRD analysis of sand revealed very similar composition in the two units (Fig. 5) with primary minerals dominating. No crystalline phosphate minerals were found in this fraction in either unit.

3.4. PCA of key variables

The PCA clearly revealed two principal components (PC_s) with eigenvalues > 1 (Kaiser index). These PC_s explained 89% of the total variance (Fig. 7). PC1 accounted for a large proportion of the variance (73%) and was dominated by the high positive loadings (0.989–0.930) of Al_{pyro}, TP and Fe_{pyro}, the moderate positive loading of P_{Meh} and the medium negative loading of pH_w. The variance of PC2 was mainly explained by Al_{amorp}, pH_w, pH_{NaF} and silt + clay fraction, which showed positive loadings between 1.072 and 0.646. All variables had communalities higher than 0.75, and variations in the transect were thus dominated by processes involving these factors. The plot of rotated variables against factor score values (FSV) of sample points (Fig. 7) shows the extent to which the samples were influenced by the components or groups of variables. Two groups of samples were clearly differentiated (see ellipses in Fig. 7). Each group corresponds to samples from each geomorphological unit, except samples EP1-1 and EP2-1, which correspond to the MT unit (Fig. 7). The group on the right is

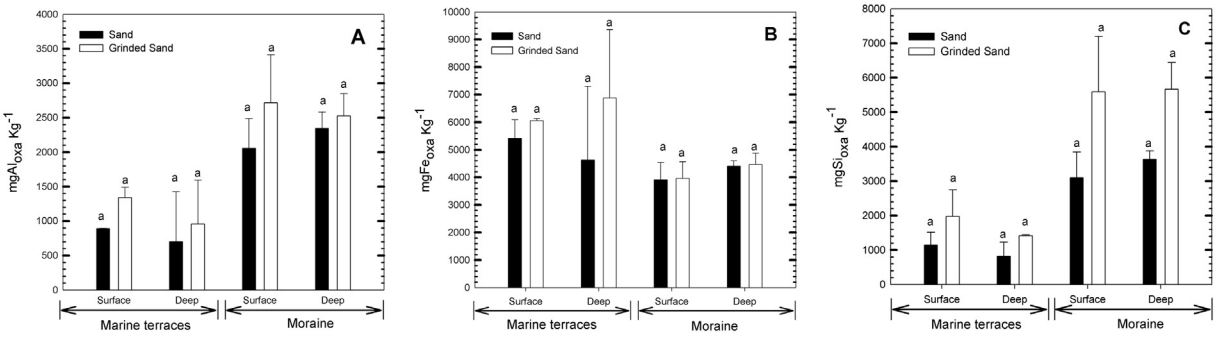

Fig. 3. Concentrations of Si, Al and Fe extracted in ammonium oxalate after simulation of glacial abrasion by grinding process. N = 2.

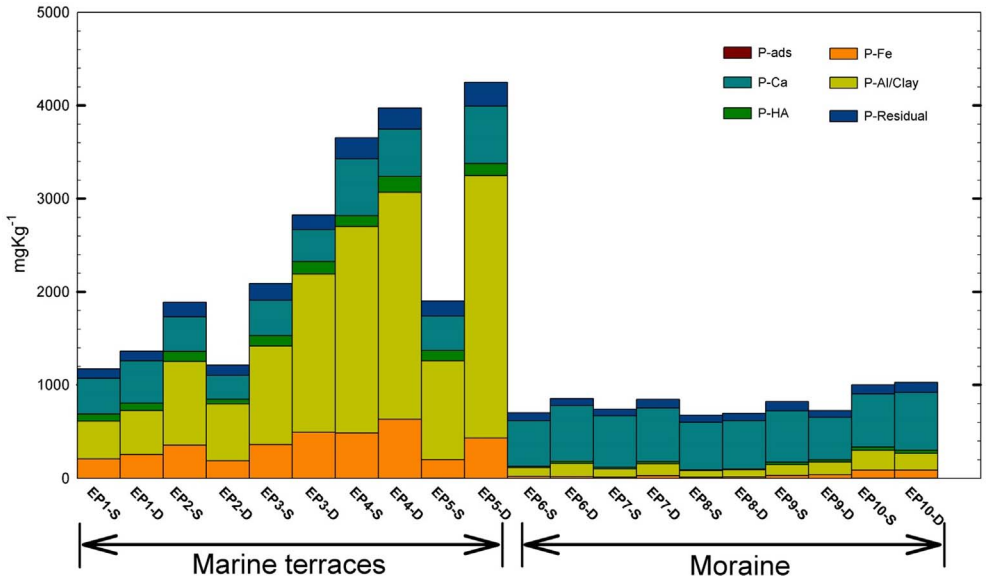

Fig. 4. Phosphorus partitioning. Deep samples are indicated by "D" and surface samples by "S".

mainly influenced by PC1, while the upper group is mainly dominated by PC2 and to a lesser extent by PC1. These results indicate that the soil properties in each unit are strongly influenced by different factors.

4. Discussion

Some authors have suggested that temperature and humidity play essential role in various soil-forming processes in cold climate and humid environments (e.g. Campbell and Claridge, 1982; Matsuoka et al., 1990), as they strongly influence freeze-thaw cycles (Henry, 2007), frost shattering (Lautridou and Ozouf, 1982) and glacial advances or retreats (Cook et al., 2005). These factors also affect edaphic processes, which are spatially very variable (Tanner et al., 2013), as well as geomorphological activity (Oliva and Ruiz-Fernández, 2017). Other authors have noted the great differences in soil properties that can be generated by the presence of seabirds and seals, which disturb the soil by trampling and by input of organic compounds in their droppings, which can accumulate to form guano and favour establishment of vegetation (Brimble et al., 2009; Otero et al., 2015b; Ugolini, 1972). The findings of the present study revealed two clearly different geochemical environments (Fig. 7). These environments are closely related to the geomorphological units studied. One of them includes the marine terrace samples and the variables affected by biota activity. In this respect, biota seems to be the main soil forming factor in marine terraces, responsible for the enrichment in nutrients and labile forms of metals and P in MT soils. The moraine environment is defined by those variables associated with geomorphological activity (Fig. 7). In the moraine, geomorphological activity seems to be the most important soil forming factor, yielding fine particles and high pH.

4.1. Biota action

Biota is an important soil-forming factor, as already described in several other Antarctica environments (Lee et al., 2004; Otero et al., 2013; Ziółek and Melke, 2014). Seabird colonies established along the coast physically and chemically modify the soil properties via the input of faecal matter and also via trampling (Bockheim, 2015; Cannone et al., 2008). In the present study, the seabird and seal colonies present on the marine terraces are the main source of organic matter, as reflected in the high values of TOC in MT (~1%) relative to values in M (~0.17%), in which organic matter may be accumulated by permafrost table and to favour the humification process. The biota is also responsible for the higher concentration of TN in MT, which is well correlated with the values of TOC. This element is more abundant in the first 10 cm of soil due to the release of faecal matter (Simas et al., 2007). Although faecal matter is initially alkaline, deposition by seabirds and seals has promoted soil acidification and leaching of base cations and enhanced microbial degradation of organic matter; this is common in cold environments where higher temperatures prevail, as in Maritime Antarctica (Bockheim, 2015).

The high concentrations of TP and P_{Meh} in MT, respectively 2 and 10 times higher than in M (Table 2), should also be interpreted as a direct effect of the seabird and elephant seal colonies on the soils. The droppings that these animals produce are rich in phosphorus com-

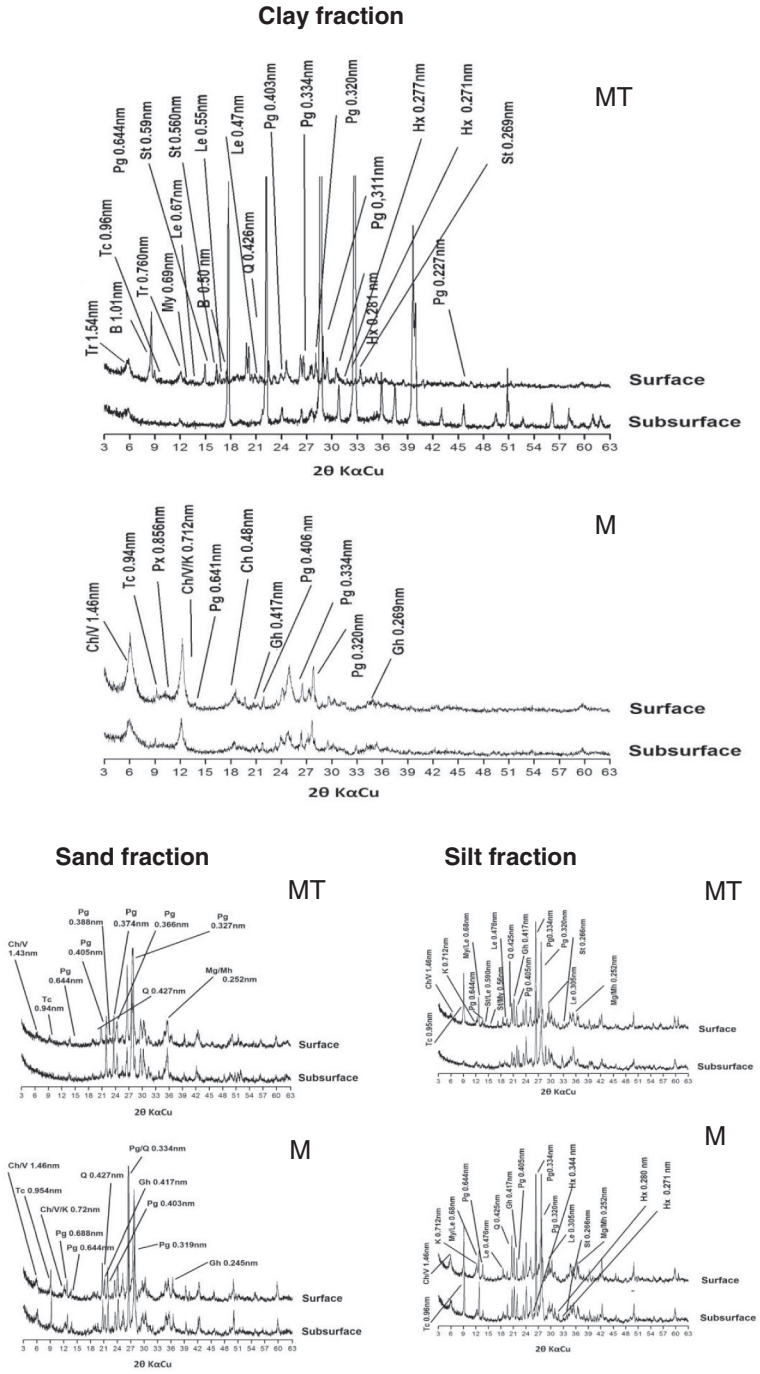

Fig. 5. XRD analysis of clay, silt and sand fraction showing minerals present in MT and M. Ch-Chlorite; V-Vermiculite; Px-Pyroxone; K-Kaolinite; B-Biotite; Pg-Plagioclases; Q-Quartz; Gh-Goethite; Hx-Hydroxylapatite; Tr-Taranakite; St-Struvite; Le-Leucophosphite and My-Minyulite.

pounds and thus substantially increase the natural fertility of the soil in the breeding areas (Anderson and Polis, 1999; Ligeza and Smal, 2003; Otero et al., 2015b; Ziółek and Melke, 2014).

The results of the mineralogical and $\delta^{15}N$ analyses are consistent with this interpretation. The MT mineralogy shows a high diversity of phosphate minerals, which are typically associated with faecal matter (Pereira et al., 2013b; Simas et al., 2007). The high concentration of P favours phosphatization processes (Tatur and Barczuk, 1985). These processes imply the formation of secondary minerals such as taranaquite $[K_3Al_5\ (PO4)_2(HPO_4)_6\ 18H_2O]$, minyulite $[KAl_2(OH,F)(PO_4)_2{\cdot}4H_2O]$, leucophosphite $[KFe_2(PO_4)_2(OH)\ 2H_2O]$, struvite $[(NH_4)Mg(PO_4)\ 6(H_2O)]$ and hydroxylapatite $[Ca_5(PO_4)OH]$ (Pereira et al., 2013a; Tatur and Myrcha, 1984), as clearly indicated by the composition of the MT clay fraction. However, hydroxylapatite may be derived from hydrated mass of decomposing faecal matter in earthy aggregates of calcium phosphate or from geological material. This occurs in the M unit (silt fraction of Fig. 5), where there is no biota, probably due to recent deglaciation, higher slope and active cryoturbation processes. Thus, hydroxilapatite is not exclusively formed as a result of phosphatization processes (Tatur and Myrcha, 1984).

The P partitioning also shows the importance of phosphatization processes in the soil, reflected in the very different distribution of P relative to that in seabird faecal matter (Otero et al., 2015b). The amount of P associated with reducible Fe and Mn oxyhydroxides was

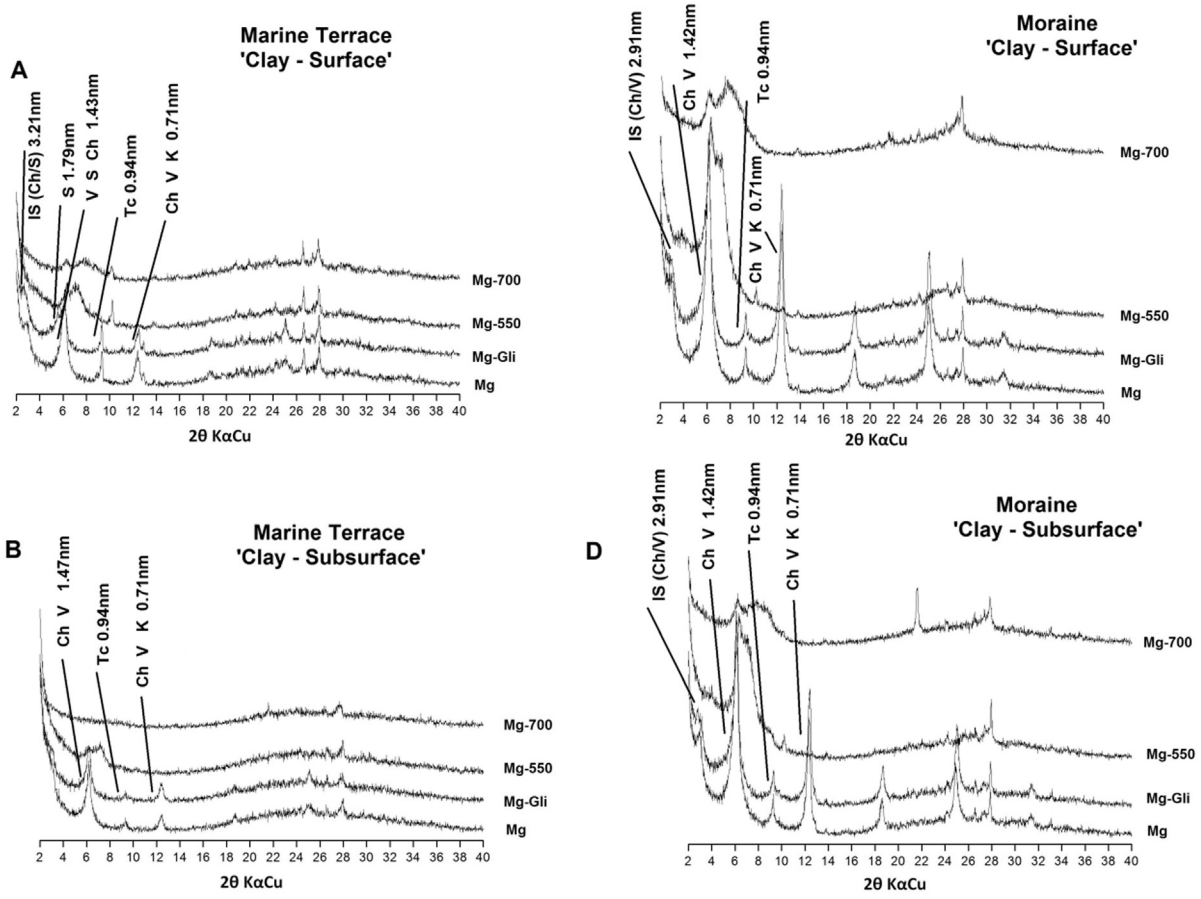

Fig. 6. XRD analysis of oriented aggregates of the clay fraction saturated with Mg^{+2} in MT and M, in surface or subsurface samples. Ch-Chlorite; V-Vermiculite; K-Kaolinite; S-Smectite; Tc-Talc and interstratified (IS) minerals as Ch/V and Ch/S.

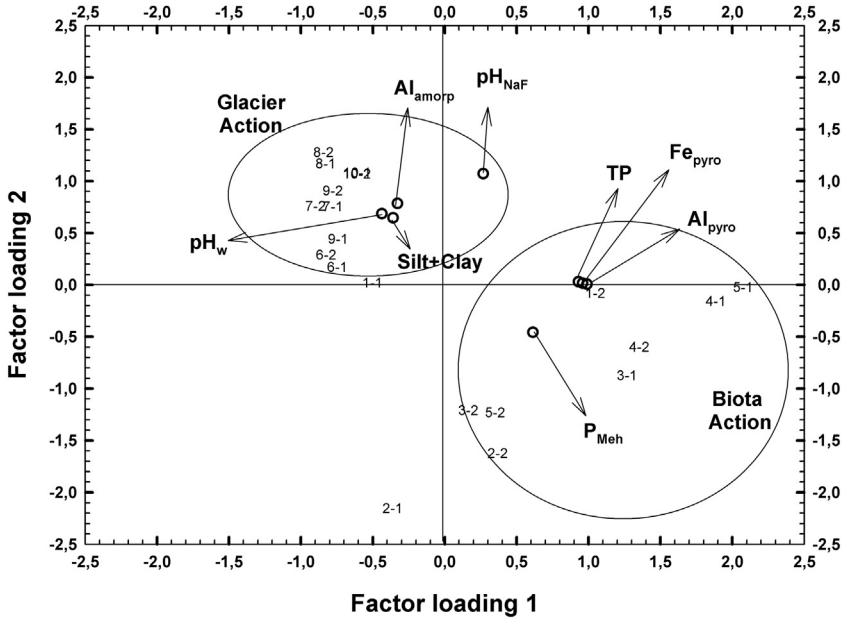

Fig. 7. Principal component analysis (PCA) of the soil variables analysed. Two groups of correlated variables and two groups of samples associated with them (indicated by ellipses) are shown.Note: Sampling points were labelled without the prefix "EP" (Elephant Point) to make them easier to read.

much higher in MT due to the low pH (Sims and Pierzynski, 2005; Wild, 1993). The P fraction associated with Al and clays (P-Al/Clay) is much more abundant in MT than in M. This is mainly because this fraction is one of the common forms in seabird faecal matter. However, this great difference between geomorphological units is presumably also due to the background level, which was higher than found in previous studies (Otero et al., 2015b; Ziółek and Melke, 2014). The P-HA also seems to be strongly related to the effect of seabirds on soil due to the higher concentration of MT (Otero et al., 2015b). The concentration of the P—Ca fraction is similar in both areas. This is a dominant fraction in

seabird excrements (Otero et al., 2015b; Ziółek and Melke, 2014), which could therefore explain the high concentration in MT unit. However, the high concentration of this fraction in M may be a consequence of the weathering of parent material and allochthonous rocks such as granodiorite, which contain apatite. Thus, allochthonous material transported from Antarctic Peninsula by icebergs (Oliva and Ruiz-Fernández, 2017) may account for the presence of struvite, leucophosphite and hydroxylapatite in the silt fraction of M and may also explain the basal level of P_{sand} (Table 2).

The isotopic composition of N in the MT unit ($\delta^{15}N$: from 13 to 17.7‰) was much higher than in M ($\delta^{15}N$: from 3 to 7.8‰), indicating different sources. The values for M are similar to those for particulate organic material (POM) (6.8 ± 0.3‰) and algae (5.1 ± 0.3‰) (Yuan et al., 2010) which can grow on the moraine. On the other hand, the high values of $\delta^{15}N$ in MT soils were similar to those obtained in soils (Mizutani et al., 1991), sediments (Liu et al., 2006; Nie et al., 2014; Yuan et al., 2010) and excrements derived from seabird and mammalian colonies ($\delta^{15}N$ = from 11.3 to 16.2‰) (Liu et al., 2006).

These findings reinforce the important influence of seabird and seal colonies (biota) have on soil formation and consequently on soil properties and composition. The presence of biota leads to input of organic matter, which changes the geochemical properties and contributes to the development of the A horizon. The biota is also responsible for other soil-forming processes such as podsolization. This process is highly incipient in Maritime Antarctica (Bockheim and Ugolini, 1990), but can be observed in different dark and grey lines in some horizons of marine terraces. This is favoured in the summer season when the ice melts on well-drained acid soil (Bockheim and Ugolini, 1990). The process is caused by the chemical migration of aluminium, iron or organic matter in depth as reflected in the values of Al and Fe extracted by pyrophosphate (Table 2). The decomposition of faecal matter also promotes acidolysis and enhances chemical weathering and plant development.

In addition to causing eutrophication of soils, waters and sediments, seabirds are also efficient vectors of seed dispersion (Calviño-Cancela, 2002), thus favouring biodiversity of the vegetation in this extreme environment (Myrcha and Tatur, 1991). In this respect, in the current scenario of climate change, plant colonization in these distant coastal areas may be accelerated by the action of seabirds, with the associated consequences, such as the increased discharge of phosphorus to the ocean, lakes or rivers (Hawkings et al., 2016).

4.2. Geomorphic action

Despite the length of time that has passed since the retreat of the glacier, the moraine sediments show evidence of intense glacial abrasion. Glaciers exert high pressure on rocks and minerals. They grind and break the substrate, thus forming finer particles (< 32 μm) (Haldorsen, 1981; Jari, 1995; Keller and Reesman, 1963b). Physical weathering explains the presence of primary minerals in clay fraction of moraine sediments and also the high pH. Glacial abrasion leads to changes in mineral structure (Fig. 5, Table 2), increasing the pH to values close to those obtained in the abrasion pH as a consequence of the release of OH groups of the crystalline structure (Gonzalez Garcia et al., 1991; Miller and Oulton, 1970; Takahashi, 1957). This loss generates amorphous minerals, e.g. of Al (Campbell and Caridge, 1987; Jari, 1995; Keller and Reesman, 1963a, 1963b; Ramesh and d'Anglejan, 1997) in the moraine. The results of the simulated glacier abrasion by grinding are consistent with this idea (Fig. 3). Unconsolidated sediments of the M unit are affected by very intense post-glacial activity of periglacial processes, particularly during the paraglacial stage (Oliva and Ruiz-Fernández, 2017). The effectiveness of cryogenic processes in the Maritime Antarctica is enhanced during the summer season when freeze-thaw cycles are frequent and moisture is abundant. This favours physical weathering processes, namely the frost-induced shattering of the boulders left by the glacier (Woronko and Pisarska-Jamrozy, 2016). This action is more intense when the grain surface is encrusted by amorphous phases (Woronko and Hoch, 2011). These processes may also explain the finer particles found in M than in MT (Campbell and Caridge, 1987), as well as the pH values close to pH abrasion and the presence of inherited primary minerals resulted from physical weathering. After the actions of the above-mentioned processes, strong winds and retreating and advancing movements of glaciers are the main causes of erosion as they move the soil material to new sites, thus contributing to the pedogenic processes as losses and additions (e.g. alluvial fans).

The absence of these properties in the MT is related to their non-glacial origin and to the horizontal surface of the terrain, which facilitates development of the vegetation cover, reducing periglacial slope processes and encouraging geomorphologic stability. The vegetation cover also limits the effects of frost on the ground and the effects of wind abrasion, which can strongly influence the geological material (Matsuoka et al., 1996) and may be another factor explaining the differences between two geomorphological units. However, more detailed studies are required to clarify the role of this weathering agent in soil formation.

Finally, the lack of any differences in the variables at the depths of soil considered can be explained by mixing of materials and homogenization of the soil profile due to cryogenic processes such as cryoturbation (Ugolini et al., 2006).

5. Conclusions

The study findings showed clear differences in soil properties and composition of marine terraces and moraine as a consequence of the biotic and geomorphic actions.

Biotic activity, driven mainly by seabird and seal colonies, seems to be the most important soil forming factor in the marine terraces. The faecal matter adds different types of organic matter, favours chemical weathering and contributes to eutrophication of the environment due to the high concentration of nutrients. Phosphatization may thus be considered the most representative soil forming process in this unit, as a consequence of the high concentration of P in faecal matter. The formation of new P minerals favours accumulation of P (and to a lesser extent N) in soils, although the increased erosion of the Antarctic coast due to ice melting may lead to eutrophication in nearby seas and lagoons.

In the moraine unit, soil formation is mainly driven by glacial abrasion. Rock abrasion destroys the crystalline structure of primary minerals, releasing Fe and Al; this leads to neoformation of secondary minerals with low degree of crystallinity and with high reactivity. This process is also driven by the alkaline reaction in moraine soils. Additionally, freeze-thaw cycles and frost shattering also contribute to the disintegration of rocks (e.g. sharp-edged clasts) and consequently generate fine particles such as silts and clays.

Finally, future studies should aim to clarify the role of geomorphological and physical processes in the development of soils in the Maritime Antarctica. Information about how glacial abrasion by grinding influences soil development is scarce. This research topic is of potential interest for advancing knowledge of soil texture, mineralogy and pH in ice-free environments. Study of the consequences of the weathering, such as the losses of Fe to the ocean is also of interest, as Fe is a limiting nutrient for primary productivity.

Acknowledgements

The authors are grateful to Maria Santiso, David Romero and Francisco Casás for help with the laboratory analysis and to Christine Helen Francis for help with revising earlier drafts of the manuscript. X.L.O. is grateful for financial support from the Proyecto PROMETEO (SENESCYT Ecuador) and Marc Oliva is grateful for funding from the project HOLOANTAR (*Holocene environmental change in Maritime*

Antarctic. Interactions between permafrost and lacustrine environment) and the Portuguese Polar Program (PROPOLAR), both from Portuguese Science Foundation. We also acknowledge the logistic support of the Brazilian and Chilean Antarctic Programs during fieldwork. Finally, A.G.G. is grateful to MINECO and FSE for the FPI pre-doctoral contract obtained through the "Programa Estatal de Promoción del Talento y su Empleabilidad en I + D + I".

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